

Empirical tolerance factor for pyrochlore structure and its correlation to the physical properties

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Abstract

In this work a new empirical tolerance factor for compounds with pyrochlore structure was proposed. This tolerance factor was suggested with basis on empirical values of structural data and the tolerance factor proposed currently. However, once it does not depends on the structural data, this new tolerance factor permit to predict some physical properties of these compounds directly.

The tolerance factor t was proposed by Goldschmidt to describe the stability and distortion in perovskite structures [1]. This is a geometrical parameter defined to the ABO_3 oxide perovskite compounds as function of the ionic radii as:

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}, \quad (1)$$

where R_A , R_B and R_O are the ionic radii of the A cation, B cation and oxygen, respectively. By definition, the tolerance factor for perovskites provides a measure of how well the A-site cation fits the twelve-fold coordinated space within the corner-shared octahedral network formed by the B-site cation. Thus, this parameter indicates how far from ideal packing can the ionic sizes from A and B cations change, with fixed size for the oxygen anion, and the structure still remains as an ideal perovskite. The value $t = 1$ indicates an ideal value, where the ions, which are considered as perfect spheres, are connected in a perfect cubic lattice. Different values from the ideal one indicate distortions in the structure with relation to the ideal perovskite, that are usually assumed as: (i) for $t > 1$, the A cations are too large to fit into their interstices and in this case hexagonal perovskites occur more frequently; (ii) for $\frac{\sqrt{2}}{2} < t < 0.9$ the A cations are too small to fit into their interstices and several possible perovskite-related distorted structures are proposed such as orthorhombic, tetragonal, monoclinic and rhombohedral ones, usually originated from BX_6 octahedra tilting to accommodate the small A cation or in some cases from Jahn-Teller distortions to get rid of degeneracies and become stable; (iii) for values lower than $t = \frac{\sqrt{2}}{2}$, when A and B cations have the same size, close-packed structures are observed, as corundum, ilmenite and KNbO_3 ones [2]. We can observe that, despite t be a simple geometrical parameter, based on the assumption of rigid spheres, it is a powerful tool in order to predict distortions in perovskite compounds. Also, useful correlations have been found between t and device-oriented physical properties of the materials. For example, Zürmühlen *et al* [3] suggested that restoring force constant of the lowest polar mode is strongly dependent on the tolerance factor, as well as the binding energy and dielectric constant of perovskites oxides. Also, the tolerance factor is correlated to the typical highest wavenumber phonon with symmetry A_{1g} active in Raman scattering, see for example [3–6]. Consequently, as the intrinsic losses are originated from phonons, they define the dielectric applicability in microwave frequency region. Thus, such features related to the tolerance factor imply in a strong dependence of these ones with the tolerance factor.

As the perovskites, oxide pyrochlores whose stoichiometry is $A_2B_2O_6O'$ (or $A_2B_2O_7$) are ternary structures that are multifunctional, serving as appropriate crystallographic host for a wide range of applications due to the great variety of possible site substitutions on both A and B sites. These substitutions imply an assortment of different physical properties, whose main one is magnetic frustration [7], but several other important such as topological Hall effect [8], metal-insulator transitions [9, 10], giant magnetoresistance [11, 12], analogous Dirac string and magnetic monopoles [13, 14], magnon hall effects [15], metallic "ferroelectricity" [16], ionic conduction [17], superconductivity [18–20], ferroelectricity [21, 22] and quantum paraelectric behavior [23] among others, are also observed. Thus, defining a tolerance factor that predicts structural and physical properties for compounds with pyrochlore-based structure is very useful.

The first tolerance factor proposed for oxide pyrochlores was defined by Isupov [24] as

$$t = 0.866 \frac{R_A + R_O}{R_B + R_O}. \quad (2)$$

To derive t , Ivunov considered the BO_6 octahedra as perfect. In the ideal pyrochlore structure $A_2B_2O_6O'$, whose symmetry belongs to the space group $Fd\bar{3}m$, considering the B cation at the origin (origin 2), the A cations and the eight oxygens O' are in special positions (A is in the $16d$ Wyckoff site with coordinates $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and the oxygen is in the $8b$ site with coordinates $(\frac{3}{8}, \frac{3}{8}, \frac{3}{8})$) and the remaining 48 oxygens are located in the $48f$ Wyckoff site with coordinates $(x, \frac{1}{8}, \frac{1}{8})$. As showed by Subramanian [25], in this structure the A cation has 8-fold coordination into a scalenohedron (distorted cube) and the B cation has 6-fold coordination into a trigonal antiprism (distorted octahedron). The oxygen independent coordinate x defines the distortion of the A and B polyhedra coordination. Geometrically, when $x = 0.3125$, the BO_6 polyhedron is a regular octahedron while AO_8 polyhedron is a distorted cube (scalenohedron), while for $x = 0.375$, the AO_8 polyhedron is an ideal cube and BO_6 is a distorted octahedra. By this way, both regular octahedron and cube is not permitted in pyrochlores. Furthermore, the limiting value for these compounds become a fluorite occurs for $x > 0.375$. Usually, the x parameter occurs between 0.309 and 0.355 and these values presuppose distorted cubes and octahedra simultaneously [25]. However, the Isupov assumption is hardly achieved in pyrochlore structure leading to incoherent tolerance factor calculations.

In order to consider the effect of essential structural features on the tolerance factor, Cai

et al [26] recently proposed two tolerance factors to describe the pyrochlore crystal structure. Cai *et al* considered the geometrical features of the different cation coordination polyhedra and proposed two distinct tolerance factors:

$$t_1 = \frac{\sqrt{\left(x - \frac{1}{4}\right)^2 + \frac{1}{32}} R_A + R_O}{\sqrt{\left(x - \frac{1}{2}\right)^2 + \frac{1}{32}} R_B + R_O} \quad (3)$$

and

$$t_2 = a \frac{\sqrt{3}}{8(R_A + R_O)}. \quad (4)$$

t_1 and t_2 Cai parameters are tolerance factors corresponding to A_2B_2 and A_4 polyhedra, respectively. In the first one the O anion is present, while in the last, the O' anion. Mainly based on the t_1 parameter, Cai *et al* proposed a stability field to distinguish pyrochlores from weberites (fluorite-related structures). Also, a relationship between the tolerance factors and dielectric properties and their applicability to analyze structure-property relations was discussed. However, both defined tolerance factors depend either on cubic lattice or on the independent oxygen position parameters. The introduction of these structural parameters turns the tolerance factors proposed by Cai *et al* more precise, but this complicates their calculations because it is necessary to measure a and x data previously to calculate the t values for pyrochlores. Although we can use theoretical estimates based on the Nikiforov [27] and bond valence sum methods [28] for these parameters, this greatly limits the structural predictions for pyrochlore compounds. In this work we derived an empirical tolerance factor for pyrochlore structure based on the t_2 tolerance factor proposed by Cai *et al* and investigated its correlation to some physical properties.

To determine the new tolerance factor we considered the dependence of the experimental lattice parameter a for several pyrochlores with the t_2 parameter proposed by Cai *et al* [26]. This behavior is shown in Figure 1 for several B ions. The data clearly follows a linear behaviour and the slopes of the curves are very close to each other. Also, the y axes intersections are driven by the B radii. In fact, from a deep analysis of the linear parameters we observe that, once the slopes are almost fixed for all B radii, it does not depend on the R_B , but it is depicted from the fit that it is nearly equal to $8R_O$. Also, as the y axes intercepts are driven by the B ion we observe it is approximately equal to $10(R_B + R_O)$. So, we can determine an expression for the a lattice parameter as function of the ionic radii after substituting the t_2 expression proposed by Cai *et al* [26]. So, the lattice parameter can

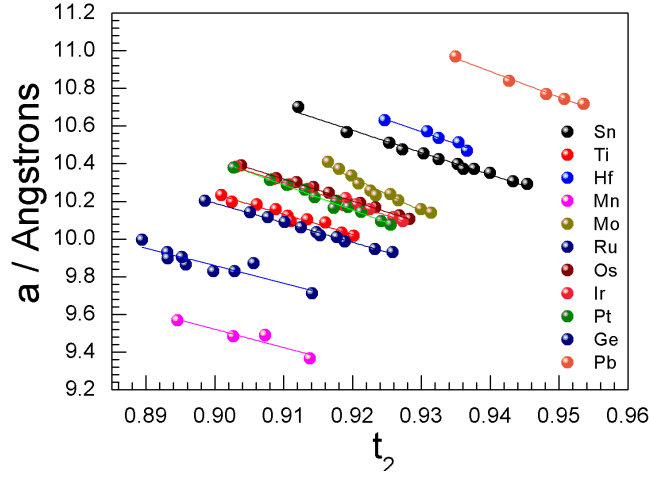


FIG. 1. Dependence of the cubic lattice parameter, a , for several pyrochlores with the t_2 parameter proposed by Cai *et al* [26]. The lines are linear fits. The spheres of the same color indicate several A ions for one specific B ion. All the linear fits performed showed $R^2 > 0.95$, with exception of Ge ($R^2 = 0.7961$), Mn ($R^2 = 0.8451$) and Hf ($R^2 = 0.9431$). This can be explained in Ge case because compounds involving Ge ions usually have high covalency degree. For compounds involving Hf and Mn, there are so few points available implying in poor adjust.

be written as:

$$a = \frac{10 (R_B + R_O) (R_A + R_O)}{R_A + (\sqrt{3} + 1) R_O} \quad (5)$$

The estimated lattice parameter shows a very well agreement with the experimental one. For to the vast majority of the compounds calculated we observe an error lower than 1.5%, that is very good for prediction. Only for compounds with Ge, which is a very small ion and that usually shows covalency, as discussed earlier, we have errors at around 3.5%. All errors calculated can be found in the Table showed in the Supplementary material.

Finally, with basis on the empirical function obtained for the lattice parameter, we can propose a new empirical equation for the tolerance factor for pyrochlore oxides compounds. So, using the Cai *et al* expression and substituting the a obtained value, we have

$$t = \frac{10\sqrt{3} (R_B + R_O)}{8 [R_A + (\sqrt{3} + 1) R_O]} \quad (6)$$

The main goal of this expression is that it does not depend on the structural parameters, although it considers the structural features in the empirical adjust of the ones. So, we

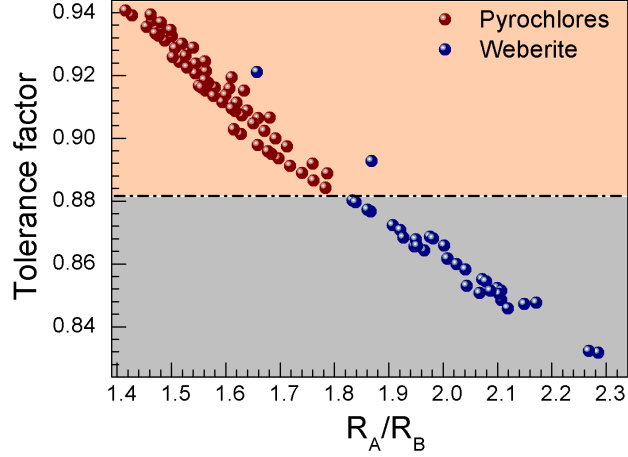


FIG. 2. Tolerance factor as a function of the A and B cations ionic radii indicating the separation between weberite and pyrochlore structure.

can predict structural and physic features of the compounds without first measuring or modeling/estimating their structural data.

One of the most important application of the tolerance factor is to estimate the structure stability field. Previously, Subramanian *et al* [25] reported for pyrochlores that the A and B ionic radii could be used to define the stability field for $A_2^{3+}B_2^{4+}O_7$, which was driven by the radii ratio, $\left(\frac{R_A}{R_B}\right)$, and the independent oxygen coordinate, x . In their work, Cai *et al* [26] used the tolerance factor t_1 to establish a stability field for pyrochlores, in order to mainly distinguish between weberites and pyrochlores structures. In this case, they obtained a good stability field, with a separation between weberites and pyrochlores. But due to the meaningless value of x for weberites, t_1 may not be the best way to distinguish pyrochlores and weberites according to the authors [26]. In Figure 2 we plot the stability field based on the new tolerance factor for compounds with pyrochlore and weberite structures. Clearly, we can distinguish between both structures. It is observed in this case that there are no problems with the absence of structural data for weberites.

In perovskites, the most remarkable correlations between the tolerance factor and physical properties are associated to the phonons and dielectric constants. Figure 3 shows the correlation between the highest infrared-active mode experimentally observed and the tolerance factor for pyrochlores compounds with $B = \text{Ti}$ and Sn . There is a full correlation with the new tolerance factor. This phonon is important because it is a bending phonon,

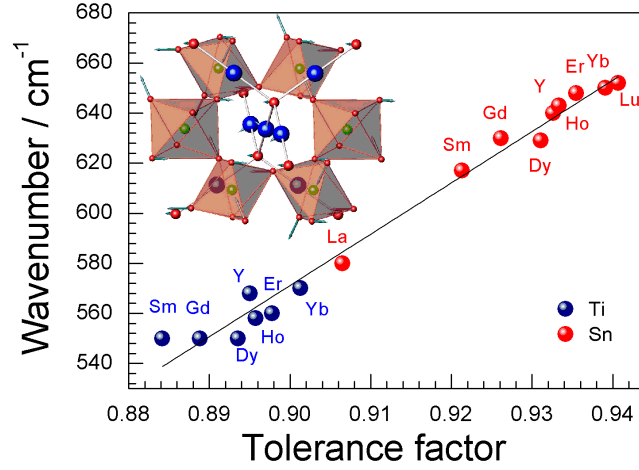


FIG. 3. Correlation between the tolerance factor and the highest infrared-active observed mode. The line indicates the linear fit with correlation of $R^2 > 0.98$. The inset shows the phonon vibration according to force field proposed by Gupta *et al* [29].

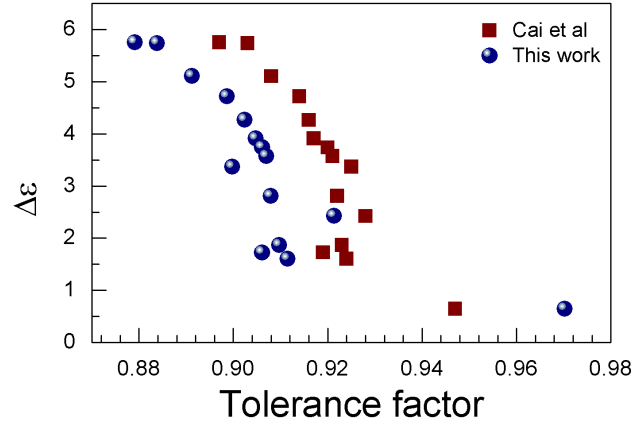


FIG. 4. Normalized permittivity difference dependence with the tolerance factor. The values calculated by Cai *et al* are also shown.

and in pyrochlores the bending phonons are directly connected to the dielectric constants. Finally, we can show that our tolerance factor exhibits the same correlation with that one proposed by Cai *et al* [26] for the normalized difference in dielectric permittivity $\Delta\epsilon_n$. This parameter is defined in terms of the measured dielectric constant, the permittivity obtained by the Clausius-Mossoti and the microscopic polarizability, α , as showed in Figure 4.

In summary, we have proposed an empirical tolerance factor for compounds with pyrochlore structure based only in the ionic radii of the constituent ions. The new tolerance factor permits a precise prediction of the lattice parameter and exhibits a strong correlation with physical properties, such as those related to the stability, phonons and dielectric constants as well as to the tolerance factor proposed for perovskite compounds.

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